

Synthesis and Characterization of a New Multi-Site Phase-Transfer Catalyst: Application in Free Radical Polymerization of Benzyl Methacrylate Under Heterogeneous Condition- A Kinetic Study

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ABSTRACT

This article presents the systematic study of kinetics and mechanism of phase-transfer catalyzed free-radical polymerization of benzyl methacrylate (BMA) in the presence of water soluble initiator potassium persulphate (PDS) coupled with 1,4-dihexadecylpyrazine-1,4-dium bromide (MPTC) in ethyl acetate/water biphasic system. The polymerization reaction was carried out under inert and unstirred conditions at a constant temperature of $70 \pm 0.1^\circ\text{C}$. The rate of polymerization (R_p) increases with increase in concentrations of BMA, PDS, MPTS. It was observed that R_p is proportional to $[\text{BMA}]$, $[\text{MPTC}]$, $[\text{K}_2\text{S}_2\text{O}_8]^{0.5}$ and (μ) independent of the ionic strength and pH of the medium. A suitable kinetic scheme has been proposed to account for the experimental observations and its significance is also discussed.

Keywords: Benzyl methacrylate, pyrazine, hexadecyl bromide, cetyl bromide, multi-site phase-transfer catalyst.

1. INTRODUCTION

The reactions between mutually insoluble reactants can be effectively conducted by phase-transfer catalysis under mild reaction conditions to get high conversion and product selectivity under mild conditions. PTC plays an important

role in organic synthesis and is widely applied in manufacturing processes of specialty chemicals, such as pharmaceuticals, dyes, perfumes, additives for lubricants, pesticides and monomers for polymer synthesis¹⁻⁵. Free radical polymerization of vinyl monomers such as butyl acrylate (BA)⁶, acrylonitrile (AN)^{7,8} methyl

methacrylate (MMA)^{9,10} glycidyl methacrylate (GMA)¹¹ butyl methacrylate (BMA)¹² and methacrylate (MA)¹³ aided by soluble single site PTCs have been reported. Although various single site PTCs are widely used for free radical polymerization¹⁴ and organic reactions, but again because of its inseparability, its usage is often limited. In order to improve the catalytic efficiency, soluble form of multisite PTC has been synthesized and used for various organic transformations especially in biphasic medium. In fact, several researchers have devoted their attention for the development of new soluble and insoluble multisite PTCs for the simple reason that they can accelerate the reactions in bi-phasic system. The first report published on multisite PTC was by Idoux *et al.*¹⁵, and they have synthesized phosphorous and quaternary onium ions containing more than one site per molecule. Various multi site PTCs have been synthesized and reported for large number of organic and polymerization reaction¹⁶⁻²⁷. In order to study the effect of change of substituent benzyl methacrylate was chosen for the study of kinetics. The present article describes the kinetics of polymerization of benzyl methacrylate in the presence of water soluble initiator under biphasic system.

2. EXPERIMENTAL

Pyrazine (Aldrich – USA), BMA (Aldrich–USA) was washed with 2% NaOH solution to remove inhibitor (HCl) and again washed with double distilled water to remove the basic impurities. The samples of potassium perdisulphate (Nice Chemicals – India) and hexadecyl bromide (SRL) were obtained from a leading dealer and other chemicals were used as received. Polyme-

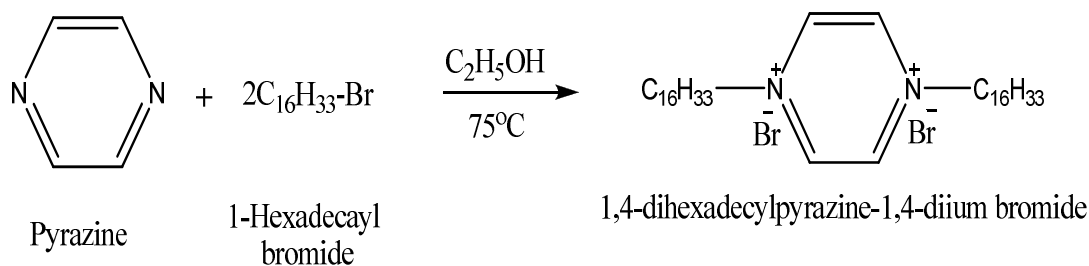
rization studies were carried out in long Pyrex tubes (4 cm X 20 cm) of about 100 ml capacity with a B-24 quick fit socket fitted with a B-24 cone with a provision for inlet and outlet terminals in order to isolate the reactive mixture from atmospheric oxygen. All other experiments were conducted in a thermostat bath of 25 liter capacity. The temperature of the bath was controlled by a hot wire vacuum switch relay to an accuracy of ± 0.1 °C. Water in the bath was heated electrically and stirred well by mechanical stirrer for maintaining constant temperature through out the bath. Experiments were carried out in the temperature range 65- 75°C. Nitrogen gas used for deaeration was freed from trace of oxygen and other impurities by passing through four vertical glass tubes containing separately (i) Fieser's solution (ii) lead acetate solution (iii) Potassium hydroxide solution and (iv) Distilled water. The FT-IR spectra were recorded on a Bruker-Tensor27 FT-IR spectrophotometer. The ¹H NMR and ¹³C NMR spectra were recorded on Bruker 500 MHZ and 125 MHZ spectrometer respectively. Elemental analysis was performed on a Perkin-Elmer 240B elemental analyzer.

SYNTHESIS OF MULTI-SITE PHASE TRANSFER CATALYST

Measured quantity of one equivalent Pyrazine dissolved in 20 mL of C₂H₅OH is taken in 250 ml two neck R_B flask. Two equivalent hexadecyl bromide is then introduced in the flask. The mixture is heated slowly for several hours. After removal of all C₂H₅OH, crystals of 1,4-dihexadecylpyrazine-1,4-diium bromide (MPTC) is obtained (scheme 1). When

washed with ether (4 x 25 mL) white crystals of MPTC was obtained.

Scheme 1; Synthesis of 1,4- dihexadecylpyrazine-1,4-dium dibromide (MPTC)



The experimental analysis data are quite satisfactory.

¹H NMR (500 MHz, CDCl₃); δ 7.33 (2H), δ 5.51 (2H), δ 4.18 (2H), δ 3.59 (2H), δ 3.28 (2H), δ 1.80 (2H), δ 1.73 (2H), δ 1.19 (2H), δ 1.11 (16H), δ 0.75 (3H).

¹³C NMR (125 MHz, CDCl₃);
 δ13.96,18.26,22.45,22.50,26.12,28.05,28.60,28.80,28.90,30.10,31.52,31.62,32.73,34.03,
 50.11, 53.05,128.68.

FT-IR (KBr,cm⁻¹); 1183 (C—N⁺ stretching), 2930 (aliphatic C—H stretching)

Elemental analysis calculated; C,62.60;H,10.21; N,4.06. **Found;**C, 62.48; H,10.12; N,3.98.

POLYMERISATION TECHNIQUE

Polymerisation reactions were carried out in the reaction tubes thermo stated at constant temperature. A known amount of monomer BMA, sulphuric acid (4M) and potassium sulphate (0.4M), and PTC were taken in the reaction tube and was flushed with purified nitrogen gas for about 30 min to ensure an inert atmosphere. A known amount of deaerated potassium perdisulphate solution thermo stated at the experimental temperature was added to the reaction mixture and simultaneously time

was noted. The reaction tubes were then carefully sealed by rubber gaskets to ensure non leakage of nitrogen gas. The reaction was arrested by pouring the content of the tube poured in ice cold methanol. The polymer was filtered out quantitatively through sintered crucible (G3) washed several times with methanol and distilled water and dried at 80 – 85°C in a vacuum oven to constant weight. The rate of Polymerisation was calculated from the weight of polymer formed using the following relationship.

$$R_p = 1000W / V t M$$

Where W - Weight of the polymer
 V - Total volume of the reaction mixture
 t - Reaction time in sec
 M - Molecular weight of monomer

It was confirmed that neither TDS nor MPTC alone initiated polymerisation under the experimental conditions employed.

3. RESULTS AND DISCUSSION

The polymerization of benzyl methacrylate (BMA) initiated by PDS-MPTC in ethyl acetate/water biphasic was studied under different experimental conditions to evaluate the various parameters which influence the polymerization reaction.

EXPERIMENTAL DETERMINATION OF STEADY STATE RATE OF POLIMERISATION

Polymerisation reactions were carried out at different time duration with fixed concentrations of BMA, MPTC, $K_2S_2O_8$, H^+ , K_2SO_4 and ionic strength (μ) to determine the steady state of polymerisation. Experimental data show that the rate of polymerisation increases initially with time, reaches a maximum and then decreases sharply to finally attain a constant value (Table-1). A plot is drawn between R_p and Time to determine the steady state rate of polymerization. It has been found from the plot (Fig-1) that the steady state rate of polymerisation is attained at about 40 min. So polymerisation was carried out 40 min duration to study the effect of other parameters.

Table-1 Study state rate of polymerization

Time (min)	$R_p \times 10^5, \text{mol.dm}^{-3}.\text{s}^{-1}$
10	7.5678
20	8.1208
30	8.867
40	9.3785
50	9.3498
60	9.3250
70	9.398

Reaction condition: [BMA], 0.2951, mol.dm^{-3} ; $[K_2S_2O_8]$, $2.0 \times 10^{-2} \text{ mol dm}^{-3}$; [MPTC], $2.0 \times 10^{-2} \text{ mol.dm}^{-3}$; $[H^+]$, 0.2 mol.dm^{-3} ; $[\mu]$, 0.05 mol.dm^{-3} ; Temp.70°C.

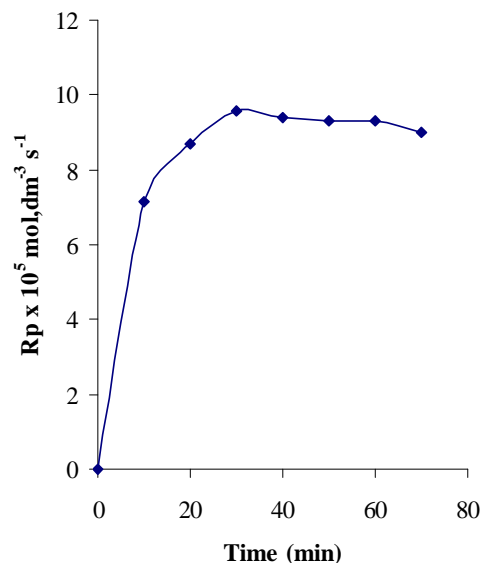


Fig. 1 : Study state rate of polymerization

Reaction condition: [BMA], 0.2951 mol.dm^{-3} ; $[K_2S_2O_8]$, $2.0 \times 10^{-2} \text{ mol.dm}^{-3}$; [MPTC], $2.0 \times 10^{-2} \text{ mol.dm}^{-3}$; $[H^+]$, 0.2 mol.dm^{-3} ; $[\mu]$, 0.05 mol dm^{-3} ; Temp.70°C

The effect of [BMA] on Rp

The effect of [BMA] on Rp was studied by conducting polymerisation with different concentrations of BMA while keeping fixed the concentrations of other components. It has been found that the Rp increased with increase in [BMA]. The plot of log [BMA] against log Rp was a straight line with a slope of 1.02 (Fig- 2). The reaction order of 1.0 with respect to [BMA] is further confirmed from the straight line passing through the origin plotted between [BMA] vs Rp. (Fig-2a). Vajiravel *et al.*, reported a first order dependence of Rp on concentration of glycidyl methacrylate in the presence of $K_2S_2O_8$ as a initiator¹¹.

Table -2 Effect of variation of [BMA] on Rp

[BMA] mol.dm ⁻³	Rp x 10 ⁵ mol.dm ⁻³ .s ⁻¹	2+log [BMA]	6+log Rp
0.2951	9.3786	1.4699	1.9721
0.5902	19.0125	1.7710	2.2790
0.8853	28.4538	1.9471	2.4541
1.1804	38.8812	2.0720	2.5897
1.4755	47.4695	2.1689	2.6764
1.7706	58.8476	2.2481	2.7694

Reaction condition : $[K_2S_2O_8]$, 2.0×10^{-2} mol.dm⁻³; [MPTC], 2.0×10^{-2} mol.dm⁻³; $[H^+]$, 0.2 mol.dm⁻³; $[\mu]$, 0.05 mol.dm⁻³; Temp.70°C; Time,40 min.

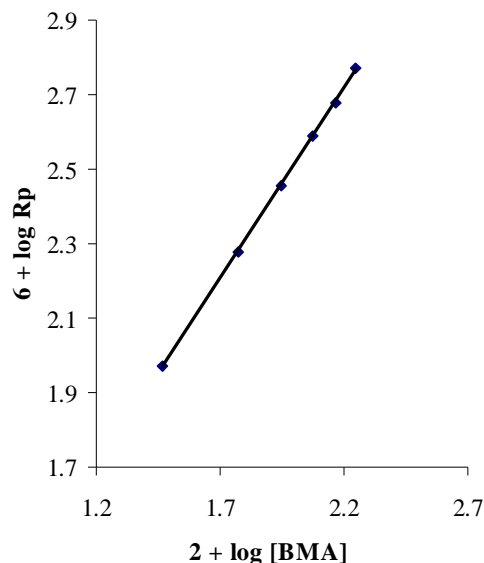


Fig. 2: Effect of variation of [BMA] on Rp

Reaction condition : $[K_2S_2O_8]$, 2.0×10^{-2} mol.dm⁻³; [MPTC], 2.0×10^{-2} mol.dm⁻³; $[H^+]$, 0.2 mol.dm⁻³; $[\mu]$, 0.05 mol.dm⁻³; Temp.70°C; Time,40 min.

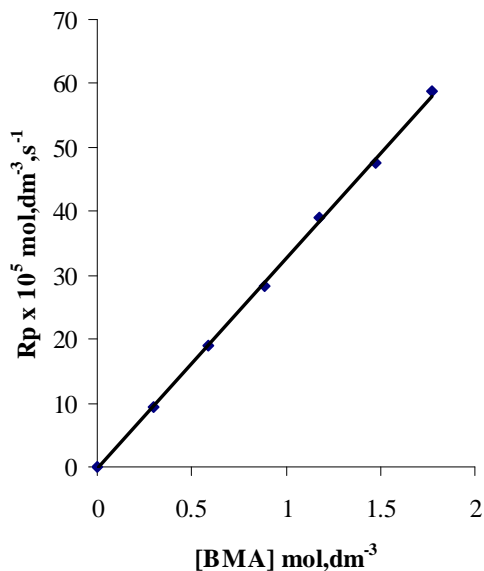


Fig. 2a : Effect of variation of [BMA] on Rp

Reaction condition : $[K_2S_2O_8]$, 2.0×10^{-2} mol.dm⁻³; $[MPTC]$, 2.0×10^{-2} mol.dm⁻³; $[H^+]$, 0.2 mol.dm⁻³; $[\mu]$, 0.05 mol.dm⁻³; Temp.70° C; Time,40 min.

Effect of $[MPTC]$ on R_p

It has been found that increasing the concentration of MPTC increases the value of R_p in the employed concentration range from 0.02 to 0.12 mol.dm⁻³ (table-3). From the plot $2+\log[MPTC]$ vs $6+\log R_p$ the slope was found to be 1.0. (Fig-3). A straight line passing through the origin in the plot of R_p vs $[MPTC]$ confirms the observed order of 1.0 (Fig-3a). Gupta and Mandal^{28,29} also reported a first order dependence of R_p on concentration of tetrabutylammonium bromide (PTC) for the polymerization of methyl methacrylate in the presence of $K_2S_2O_8$ in ethyl acetate/water media.

Table-3 Effect of variation of $[MPTC]$ on R_p

$[MPTC] \times 10^2$ mol.dm ⁻³	$R_p \times 10^5$ mol.dm ⁻³ .s ⁻¹	$2+\log$ $[MPTC]$	$6+\log R_p$
2	9.3786	0.3010	1.9721
4	21.3814	0.6010	2.3300
6	37.4290	0.7781	2.5732
8	47.1201	0.9030	2.6732
10	54.0886	1.0000	2.7331
12	67.9369	1.0792	2.8321

Reaction condition : $[BMA]$, 0.2951 mol.dm⁻³; $[K_2S_2O_8]$, 2.0×10^{-2} mol.dm⁻³; $[H^+]$, 0.2 mol.dm⁻³; $[\mu]$, 0.05 mol.dm⁻³; Temp.70° C; Time, 40 min.

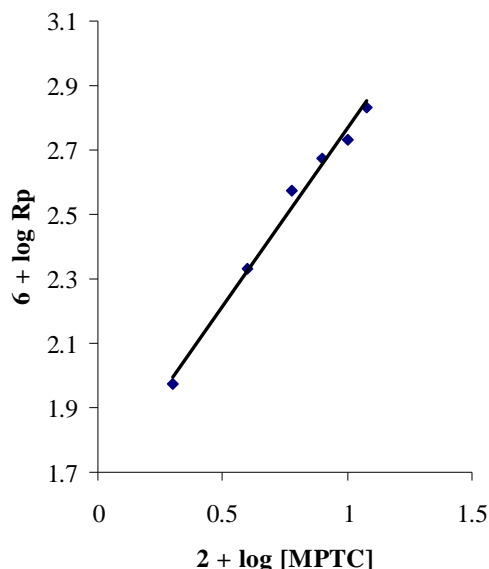


Fig.3 : Effect of variation of $[MPTC]$ on R_p

Reaction condition : $[BMA]$, 0.2951 mol.dm⁻³; $[K_2S_2O_8]$, 2.0×10^{-2} mol.dm⁻³; $[H^+]$, 0.2 mol.dm⁻³; $[\mu]$, 0.05 mol.dm⁻³; Temp.70° C; Time, 40 min.

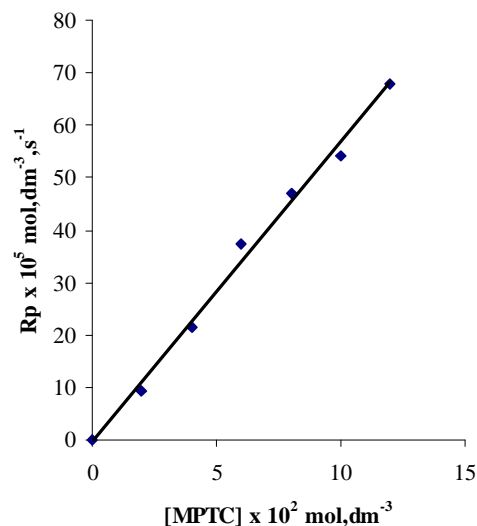


Fig.3a : Effect of variation of $[MPTC]$ on R_p

Reaction condition : [BMA], 0.2951 mol.dm⁻³; [K₂S₂O₈], 2.0 x10⁻² mol.dm⁻³; [H⁺], 0.2 mol.dm⁻³; [μ], 0.05 mol.dm⁻³; Temp.70°C; Time, 40 min.

Effect of [PDS] on Rp

The effect on Rp of varying the concentration of K₂S₂O₈ was observed by varying concentration in the range of 0.02 to

0.12 mol.dm⁻³ at a fixed concentration of BMA, MPTC, H⁺ and ionic strength (μ) (Table-4). It is found that Rp increase with increase in the concentration of PDS. A plot of log Rp vs log [K₂S₂O₈] is linear with a slope of 0.5, indicating the half order dependence of Rp on K₂S₂O₈ (Fig-4). This is supported by a straight line passing through origin in the plot of Rp vs [K₂S₂O₈] (Fig-4a).

Table-4 Effect of variation of [PDS] on Rp

[PDS]x10 ² mol.dm ⁻³	{[PDS]x10 ² } ⁻⁵ mol.dm ⁻³	Rpx10 ⁵ mol.dm ⁻³ .s ⁻¹	2+log[PDS]	6+logRp
2	0.1414	9.3786	0.3010	1.9721
4	0.2000	14.6094	0.6010	2.1646
6	0.2449	15.9712	0.7781	2.2033
8	0.2828	18.0026	0.9030	2.2553
10	0.3162	22.6743	1.0000	2.3553
12	0.3464	23.5144	1.0792	2.3713

Reaction condition : [BMA], 0.2951; mol.dm⁻³; [MPTC], 2.0 x10⁻²; mol.dm⁻³; [H⁺], 0.2 mol.dm⁻³; [μ], 0.05 mol dm⁻³; Temp.70°C; Time, 40 min

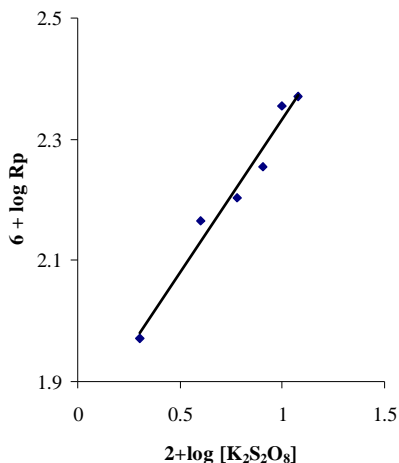


Fig.4 : Effect of variation of [PDS] on Rp

Reaction condition: [BMA],0.2951; mol.dm⁻³; [MPTC], 2.0 x10⁻²; mol.dm⁻³; [H⁺], 0.2 mol.dm⁻³; [μ], 0.05 mol dm⁻³; Temp.70°C; Time, 40 min

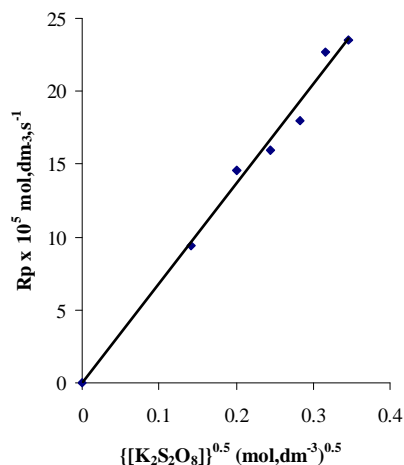


Fig.4(a) : Effect of variation of [PDS] on Rp

Reaction condition: [BMA], 0.2951; mol.dm⁻³; [MPTC], 2.0 x10⁻²; mol.dm⁻³; [H⁺], 0.2 mol.dm⁻³; [μ], 0.05 mol dm⁻³; Temp.70°C; Time, 40 min.

Effect of temperature on Rp

The polymerization was carried out at different temperatures, i.e., 333, 338, 343, and 348 K at definite concentrations of BMA, $K_2S_2O_8$, MPTC, H^+ and ionic strength. The rate of polymerisation increases with temperature. The activation

energy for the overall rate of polymerisation has been computed from the Arrhenius plot of $\log R_p$ vs $1/T$ (Fig-5) and it was found to be $9.901 \text{ kcal.mol}^{-1}$. The thermodynamic parameters such as ΔS^\ddagger , ΔH^\ddagger and ΔG^\ddagger have also been calculated from the Eyring plot of $\log R_p/T$ vs $1/T$ and are presented in Table-5.

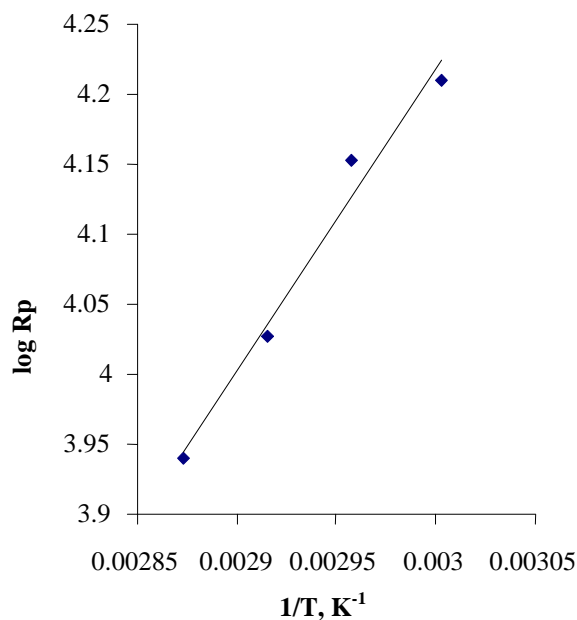


Fig. 5 : Effect of change of temperature on Rp

Reaction condition : [BMA] , $0.2951 \text{ mol.dm}^{-3}$; [MPTC], $2.0 \times 10^{-2} \text{ mol.dm}^{-3}$; [$K_2S_2O_8$], $2.0 \times 10^{-2} \text{ mol.dm}^{-3}$; [H^+], 0.2 mol.dm^{-3} ; [μ], 0.05 mol.dm^{-3} ; Time, 40 min.

Table 5 Thermodynamic parameters

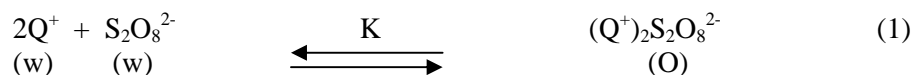
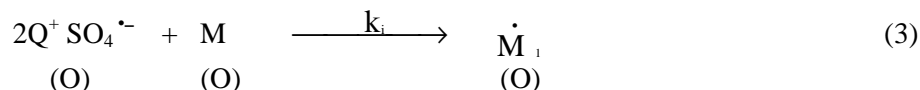
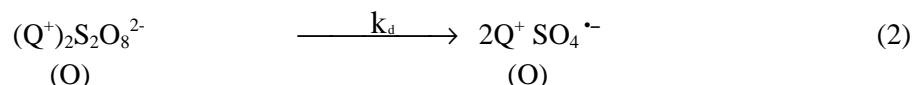
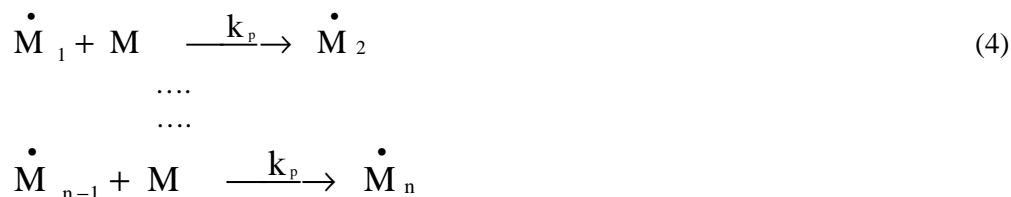
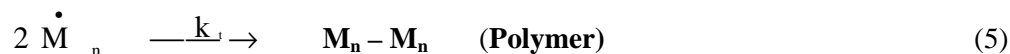
Ea, kcal.mol^{-1}	ΔH^\ddagger , kcal.mol^{-1}	ΔS^\ddagger , eu	ΔG^\ddagger , kcal.mol^{-1}
9.91	9.19	-43.94	24.26

Effect of H^+ and ionic strength on R_p

It was observed that there is no discernable effect on rate of polymerization by changing the acid strength (H^+) and ionic strength (μ) of the medium.

4. MECHANISM AND RATE LAW

A mechanism has been proposed to explain the above mentioned experimental observations.

(a) Phase Transfer**(b) Initiation****(c) Propagation****(d) Termination**

The subscripts (o) and (w) refer to organic phase and aqueous phase, respectively. Where K is equilibrium constant, k_d is the reaction rate constant of decomposition, k_i is the reaction initiation rate constant, k_p is the reaction rate constant of propagation, and k_t is the reaction rate constant of termination. Q^+ refers to the

catalyst. This mechanism involves the formation of quaternary ammonium perdisulfate complex in the aqueous phase $[(Q^+)_2S_2O_8^{2-}]$, which is then transferred to the organic phase. The decomposition of the ion-pair takes place in the organic phase leading to the formation of $2Q^+SO_4^{\bullet-}$.

Applying the general principles of the radical polymerization and stationary state hypothesis to the radical species, the rate law for this mechanism can be derived as:

$$R_p = k_p \left(\frac{k_d K}{k_t} \right)^{1/2} \frac{[M][S_2O_8^{2-}]^{1/2}[Q^+]_{Total}}{1 + K[Q^+]_w[S_2O_8^{2-}]_w}$$

The above equation satisfactorily explains all the experimental observations.

5. CONCLUSION

The kinetic parameters such as rate of polymerization R_p of free radical polymerization of benzyl methacrylate, increases with increasing concentration of monomer, initiator, catalyst and temperature. The pH and ionic strength μ are independent to R_p .

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